



PATENT SPECIFICATION

NO DRAWINGS

939,244

Date of Application and filing Complete Specification Nov. 25, 1959.

No. 40117/59.

Application made in Germany (No. F27113 IVb/39c) on Nov. 25, 1958.

Complete Specification Published Oct. 9, 1963.

© Crown Copyright 1963.

Index at acceptance:—Classes 70, E62C; and 2(6), P2D1(A:B:X), P2K(7:8), P2T1(C:X), P7D1(A:X), P7K2, P7T1(C:X).

International Classification:—C08c.

COMPLETE SPECIFICATION

High Molecular Weight f Process for the Isolation of Substances o from solutions thereof

WE, FARBWERKE HOECHST AKTIENGESellschaft vormals Meister Lucius & Brüning, a body corporate recognised under German law, of Frankfurt(Main)-Höchst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for isolating rubber-like substances of high molecular weight from solutions thereof.

It is known that polymers or copolymers having a more or less rubber-like nature and that are soluble in organic solvents, such as heptane, benzene or toluene, can be obtained by polymerizing or copolymerizing olefines, for example, by the Ziegler-type process described in British Specifications Nos. 799,392, 799,823, 801,031, 794,359, 819,857 and 852,639. The starting materials used for making these products are straight or branched α -olefines or diolefines containing from 2—12 carbon atoms, which may be used alone or in admixture with one another, for example, propylene, butylene or isoprene, or mixtures of ethylene with propylene, ethylene with butylene, ethylene with butylene and isoprene.

The polymeric olefines which are obtained in solution in the polymerization medium, have hitherto been isolated by precipitation with methanol, whereby, in most cases a large sticky lump still containing solvent is obtained which is difficult to remove from the reaction vessel.

It is also known that chlorinated rubber can be isolated from solutions thereof in organic solvents by slowly running these solutions into an aqueous precipitation bath which may contain a wetting and/or emulsifying

agent while simultaneously distilling off the solvent, and taking care that the precipitated chlorinated rubber is immediately removed from the precipitation zone.

A process has also been described wherein vinyl compounds can be polymerized in aqueous suspension in the presence of a hydrophilic, semicolloidal clay, for example, a bentonite or colloidal alkaline earth metal carbonate or barium dimethyl carbonate or barium sulphate, so as to prevent the polymer particles from agglomerating and so as to obtain bead-like polymers having substantial a uniform particle size. When, however, the polymerisation baths contain an organic emulsifier, the polymers obtained have a lower stability to light and heat.

The present invention provides a process for the isolation of a rubber-like polymer as hereinafter defined, from a solution thereof in an organic solvent without the formation of lumps and without the light and heat stability and the good mechanical properties thereof being impaired, which comprises gradually introducing the solution into an excess of water which is heated to a temperature between 45° C and its boiling point in the presence of a finely divided water-insoluble solid material and, as organic surface active emulsifying agent, a hydroxy-ethylated stearic alkyl phenol, a hydroxy-ethylated stearic alcohol, dodecylbenzene sulphonic acid, an alkali metal salt of dodecylbenzene sulphonic acid, an alkylsulphonate, a condensation product from a fatty acid chloride with a β -hydroxyethane-sulphonic acid, a condensation product from a fatty acid chloride with methyltaurine, dodecylbenzyltrimethyl ammonium chloride, octadecyltrimethyl ammonium chloride, didodecyltrimethyl ammonium chloride, dodecylaminoacetate, oleylamino-

[Price 4s. 6d.]

acetate, triisobutylphenol, sorbitol mono-laurate, oleyl alcohol, octyl alcohol, oleic acid, ricinoleic acid, a reaction product of coconut fatty acids and 2 mols. dialkanol amine or a reaction product of an amide of a hydrogenated stearic fatty acid having 6-50 mols ethylene oxide, distilling off the solvent, and separating the resulting particles of the polymer material from the water. The term "rubber-like polymers" is used herein as meaning a copolymer of ethylene and propylene, a copolymer of ethylene, propylene and butadiene polyisoprene, polybutylenes, polybutadienes, copolymers of butadiene and styrene, or butadiene and acrylonitrile, or a factice.

As finely dispersed water-insoluble solid materials, there may be used the compounds of the metals and metalloids of Groups II-V of the Periodic Table in the form of their water-insoluble oxides, hydroxides or salts, for example, as the sulphates, carbonates, salts or organic carboxylic acids or especially as the silicates thereof. As such compounds there may be used, for example, magnesium carbonate, aluminium hydroxide, aluminium oxide or finely dispersed barium sulphate, silicon dioxide or silica gel, lead oxide (litharge), an antimony oxide, zinc stearate or the zinc salt of 2-ethyl-hexylic acid, titanium dioxide, or especially an aluminium silicate, for example, a commercial bleaching earth, bentonite or attapulgus clay.

It is especially advantageous to add to the water a substance which would otherwise have to be added to the precipitated polymer during the processing treatment. In this way, a separate mixing process can be dispensed with. Thus, for example, finely divided zinc stearate, lead oxide or other processing assistant or stabilizer and an anti-ageing agent or substance necessary for the subsequent finishing or vulcanisation of the polymer, for example, scot, sulphur or metal sulphide, may be mixed with the water used for the precipitation of the polymer.

The organic surface active emulsifying agents may be used alone or in admixture with one another. Examples of alkyl sulphates that may be used as the emulsifying agent are alkyl sulphates based on substantially linear Diesel oil fractions containing from about 10-20 carbon atoms and boiling at a temperature within the range of about 250 to 300° C, and that have been prepared by sulphochlorination and saponification with an alkali. As examples of condensation products of fatty acid chlorides that may be used, there may be mentioned oleic acid chloride, with β -hydroxyethane-sulphonic acid or with methylaurine.

The finely divided water insoluble solid material and the surface-active agents are each advantageously used in a proportion ranging from about 0.1-10%, preferably

0.5-2% by weight calculated on the amount of rubber-like polymers to be isolated. The ratio of water insoluble material to surface-active agent may range from 1:10 to 10:1, preferably 1:2 to 2:1. In special cases, the amount of these additives or the ratio of one to the other used may be above or below the range indicated above.

The above solids and/or surface-active substances may be added to the water used for precipitation or, alternatively, they may be wholly or partially added to the organic solution of the polymer to be isolated in which solution the polymerisation has been carried out, for example, in hexane, heptane, benzene, toluene, or xylene. The solvent used may also be a petroleum or Fischer-Tropsch Diesel oil fraction boiling within the range of about 50° to 250° C, which fractions have advantageously been previously freed from unsaturated constituents by hydrogenation, a paraffinic oil, halogenated hydrocarbon, for example, carbon tetrachloride, carbon tetrabromide, trifluorobromomethane, trifluorochloromethane, trichlorobromomethane, trichlorochloromethane, dichlorodifluoromethane, dibromodifluoromethane, dichlorodibromomethane, chloroform, bromoform, methylene chloride, methylene bromide, 1:2 - dichloroethane, 1:2 - dibromoethane, 1:1:1:2 - tetrachloroethane, 1:1:1:2 - tetrabromoethane, symmetrical tetrachloro- and tetrabromosthane, or a halogenopropane, halogenobutane, or *n*-butyl chloride, *n*-butyl bromide, isobutyl chloride, isobutyl bromide, tert-butyl chloride, tert-butyl bromide, tert-amyl bromide or *n*-hexyl bromide. The solution that is introduced into the hot water may have been pre-emulsified with water.

The process of this invention may be carried out under atmospheric pressure at a temperature within the range of 45° C-100° C, the temperature depending on the boiling point of the solvent used; it may also be carried out under super-atmospheric or sub-atmospheric pressure, is desired, at a correspondingly lower or higher temperature.

During the precipitation of the substance, it is advantageous to keep the organic solution thereof and the precipitation water in rapid motion by means, for example, of a high-speed stirrer. In this way, the precipitated product is rapidly removed from the precipitation zone and any tendency for the particles to agglomerate is further reduced.

The precipitation process of this invention may be carried out in a known apparatus, in a continuous or discontinuous manner, for example, in a vessel provided with a stirrer, with or without a continuous overflow, or in an apparatus of the type disclosed in French Specification No. 1,189,651, U.S. Specification No. 2,592,814 or in British Specifications Nos. 422,192, 418,069 and 435,726; 130

(cf. also A. Nielsen "Chlorkautechuk" (1947), pages 26-27).

The process is generally carried out under neutral conditions in water, or it may, however, be carried out in the presence of a substance of acid or alkaline reaction. If it is desired to keep the aqueous phase at a constant pH-value, a buffer may be added thereto, for example, a mixture of boric acid and a borate, or a mixture of acetic acid and an acetate.

The present invention has the special advantage that water-soluble constituents and impurities, especially water-soluble conversion products of Ziegler-type catalysts, which may be formed during the polymerization, can be removed without necessitating a special operation. The presence of these catalysts in the final polymeric substance often impairs the properties of the product.

The process of this invention has the further advantage that the small particles of the polymer can be readily isolated from the hot or cooled aqueous suspension which is finally obtained free from organic solvents. This isolation may be carried out most simply by filtration, for example, on a suction filter, a flat filter, plate filter or rotating filter. Any other known method may also be used such, for example, as decanting, centrifuging or atomizing-drying.

In contradistinction to the known polymer precipitation method, which requires the addition of methanol, the present invention has the advantage that no substantial proportion of methanol is required. The use of methanol for this purpose results in the precipitation of compact masses, which are difficult to remove from the reaction vessel and which may retain substantial quantities of solvent.

Belgian Specification No. 557,454 describes a method whereby solutions of polyolefines in low-boiling organic solvents are introduced into warm water in such a manner that the organic solvent is thereby evaporated. However, it has been found that the olefine polymers so obtained tend to agglutinate under such conditions, so that the separation and recovery of the pure polymer involves considerable mechanical difficulties. According to the process of the present invention, on the other hand, a compact mass formation is avoided, the polymeric substance separates in a pulverulent or gritty form and, therefore, it is substantially easier to obtain in a pure state simply by filtration and washing.

The following Examples illustrate the invention:

EXAMPLE 1:

150 litres of water, 250 gms of commercial aluminium hydrosilicate (breaching earth), and 200 grams of commercial hydroxyethylated octyl phenol (8 glycolic ether units) were introduced into a 300-litre

vessel provided with a descending cooler, a thermometer, a stirrer, a supply line for hot water and an inlet tube projecting for a short distance into the apparatus and the aqueous medium was then heated to 95° C. A solution of 20 kgs of an amorphous ethylene-propylene copolymer (60:40 mol%) prepared under atmospheric pressure with a Ziegler-type catalyst of $\text{VO}(\text{C}_2\text{H}_5)_3$ and aluminium diethyl monochloride (η red: 3.2 measured as a 0.5% solution in tetrahydronaphthalene at 130° C), in 180 litres of toluene was supplied from a second vessel and forced onto the hot aqueous medium by means of nitrogen. The copolymer solution was introduced at the same rate at which the toluene plus water distilled off. During the distillation, about 180 litres of hot water were added in 3-4 portions to replace the water distilled off with the toluene. After the polymer solution had been stirred in, stirring was continued at 90-95° C until no more toluene distilled off. The aqueous suspension was then cooled to 50-60° C and filtered under suction. The amorphous copolymer obtained on the filter was washed with hot water and then dried at 60-70° C under sub-atmospheric pressure 20 kgs of a colourless, gritty ethylene-propylene copolymer were obtained.

Instead of using hydroxyethylated octyl phenol, there may be used 220 grams of the sodium salt of dibutynaphthalene sulphonate, or 225 grams of an alkyl sulphonate prepared from a Diesel oil fraction having a boiling range of 250° to 300° C and containing up to about 18 carbon atoms by sulphonchlorination and alkaline hydrolysis.

EXAMPLE 2:

An apparatus as used in Example 1 but equipped with a high speed stirrer, was charged with 150 litres of water. 200 grams of bentonite and 200 grams of a commercial hydroxyethylated diisobutylphenol were then added at 80-90° C, while stirring. A solution of 15 kgs of an amorphous ethylene-propylene copolymer (45:55 mol %), prepared under atmospheric pressure with a Ziegler-type catalyst comprising VOCl_3 and aluminium triisobutyl (η red: 2.2, measured as a 0.5% solution in tetrahydronaphthalene at 130° C), in 160 l. benzene was gradually introduced at 80-90° C in the manner described in Example 1; the addition of the copolymer was so regulated that the water temperature was held at or above 75° C. The water which distilled off with the benzene was replaced portionwise. After the copolymer solution had been stirred in and no more benzene distilled off, the copolymer suspension was cooled and transferred to a narrow mesh sieve or a flat filter. The precipitated copolymer was obtained in gritty form. After drying at 60-70° C under reduced

pressure, the yield of copolymer was 15 kg.

Instead of benzene there may be used the same amount of an aliphatic benzine mixture boiling at 60–80° C, or the same quantity of chlorobenzene, cyclohexane, pentane or methylene chloride.

Instead of the hydroxyethylated alkylphenol there may be used the same amount of a hydroxyethylated naphthol or a hydroxyethylated wax alcohol containing from 10–16 glycolic ether units.

EXAMPLE 3:

An apparatus as used in Example 2 was charged with 150 litres of water, 225 gms of zinc stearate, and 150 gms of a commercial hydroxyethylated octyl phenol (9 glycolic ether units) and the whole was stirred at 95° C. Stirring was continued while a solution of 15 kgs of an amorphous ethylene-propylene copolymer (65:35 mol %) (η red: 1.8, measured as a 0.5% solution in tetrahydronaphthalene at 130° C) in 170 litres of toluene was run in, in the manner described in the preceding Examples. After all the toluene had distilled off, the suspension was cooled and filtered under suction. The fine, sandy amorphous copolymer obtained on the filter was washed with water at 60° C, and then dried under reduced pressure. The yield was 15 kg.

Instead of the hydroxyethylated octyl phenol there may be used 100 gms of oleic acid methyl tauride, to give the same good results.

EXAMPLE 4:

An apparatus as used in Example 2 was charged with 150 litres of water, 200 gms of silica gel, and 200 gms of a commercial hydroxyethylated stearyl alcohol (8 glycolic ether units), and the whole was stirred at 95° C–100° C. A solution of 15 kg of an amorphous copolymer (ethylene, propylene, and butadiene 60:30:10 mol %) (η red: 2.0 measured at 0.5% solution in tetrahydronaphthalene at 130° C) prepared with a catalyst comprising VCl_4 and $\text{Al}(\text{C}_2\text{H}_5)_3$, in 200 litres of chlorobenzene was introduced, while stirring, at the same rate as that at which the chlorobenzene distilled off. The water lost by codistillation with the chlorobenzene was replaced by adding hot water portionwise. After all the chlorobenzene had distilled off, the suspension was cooled, filtered under suction washed with hot water and dried at 60–70° C under sub-atmospheric pressure. 15 kg of a sandy, amorphous copolymer were thus obtained.

EXAMPLE 5:

A 20-litre vessel provided with a high speed stirrer, a descending cooler, a thermometer, an inlet for the dissolved material, and a hot water inlet was charged with 10 litres of

water at 90–95° C containing 15 grams of aluminum hydrosilicate (breaching earth), 10 gms of phenyl- β -naphthylamine, and 10 grams of hydroxyethylated octyl phenol (8 glycolic ether units). 1 kg of a polyisoprene (η red: 1.7 measured as a 0.5% solution in tetrahydronaphthalene at 130° C) and prepared with the aid of a catalyst comprising TiCl_4 and $\text{Al}(\text{C}_2\text{H}_5)_3$ in 10 litres of toluene was gradually introduced at 90–95° C, while stirring, at the same rate as that at which the toluene distilled off. After all the toluene had distilled off, the suspension was cooled, filtered under suction, washed with cold water and finally dried at 60–70° C under sub-atmospheric pressure. 1 kg of a sandy polyisoprene, stabilized against ageing, was thus obtained.

A polyisoprene consisting substantially of the cis-1:4-isomer and prepared in the manner described in German Specification 1,040,795 or 1,040,796 in the presence of a lithium catalyst can be isolated from its solution, in a stabilized form, in the manner described above. The process described in the above Example can also be used for isolating a copolymer of butadiene and styrene from a solution thereof.

Instead of the hydroxyethylated octyl phenol there may be used the same amount of dodecylbenzyltrimethyl ammonium chloride or of a condensation product obtained from coconut fatty acid with 2 molecular proportions of diethanolamine, or 15 grams of a hydroxyethylated octyl alcohol having 25 ethylene oxide units, to give the same good results.

WHAT WE CLAIM IS:—

1. A process for the isolation of a rubber-like polymer as hereinbefore defined from a solution thereof in an organic solvent, which comprises gradually introducing the solution into an excess of water which is heated to a temperature between 45° C and its boiling point in the presence of a finely divided water-insoluble solid material and, as organic surfaces active emulsifying agent, a hydroxyethylated alkyl phenol, a hydroxyethylated stearic alcohol, dodecylbenzene sulphonic acid, an alkali metal salt of dodecylbenzene sulphonic acid, an alkylsulphonate, a condensation product from a fatty acid chloride with a β -hydroxyethane-sulphonic acid, a condensation product from a fatty acid chloride with methyltaurine, dodecyl-benzyltrimethyl ammonium chloride, didodecyltrimethyl ammonium chloride, dodecylaminoacetate, oleylaminoacetate, triisobutylphenol, sorbitol monolaurate, oleyl alcohol, octyl alcohol, oleic acid, ricinoleic acid, a reaction product of coconut fatty acids and 2 mols dialkanol amino or a reaction product of an amide of a hydrogenated stearic

- fatty acid having 6—50 mols ethylene oxide, distilling off the solvent, and separating the resulting particles of the polymer material from the water.
- 5 2. A process as claimed in Claim 1, wherein the temperature of the aqueous medium is within the range of 45° C—100° C.
3. A process as claimed in Claim 1, wherein the aqueous medium contains 0.1—10% by weight, calculated on the amount of rubber-like polymer used, of the finely divided water insoluble solid material and 0.1—10% by weight of the organic surface active emulsifying agent.
- 10 4. A process as claimed in any of Claims 1—3, wherein the aqueous medium contains 0.5—2% by weight, calculated on the amount of rubber-like polymer used, of the finely divided water insoluble solid material and 0.5—2% by weight of the organic surface active emulsifying agent.
- 15 5. A process as claimed in any one of claims 1—4, wherein the finely divided water insoluble material used is magnesium carbonate, aluminium hydroxide, aluminium oxide, barium sulphate, silicon dioxide, silica gel, lead oxide, antimony oxide, zinc stearate, a zinc salt of 2-ethyl-hexylic acid, titanium oxide, or an aluminium silicate.
6. A process as claimed in any one of claims 1—5, wherein the removal of the granular product is carried out by means of a high-speed stirrer.
7. A process as claimed in any one of claims 1—6, wherein a processing assistant, stabiliser, vulcanising agent and/or an anti-aging agent is added to the aqueous medium during the isolation of the granular product.
8. A process as claimed in any one of claims 1—7, wherein a compound having an acid, alkaline or buffering action is added to the aqueous medium used for the isolation of the rubber-like substance.
9. A process for the isolation of rubber-like polymers as hereinbefore defined, conducted substantially as described in the Examples herein.
10. Rubber-like polymers as hereinbefore defined, whenever obtained by the process claimed in any one of Claims 1—9.
- ABEL & IMRAY,
Chartered Patent Agents,
Quality House, Quality Court,
Chancery Lane, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1963.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.